

WHAT IS CLAIMED IS:

1. A method for preparing a β -hydroxycarboxylic acid ester comprising reacting a β -hydroxycarboxylic acid, or salt thereof, with an alcohol in the presence of an esterification catalyst and the absence of solvent other than the alcohol under substantially anhydrous conditions at atmospheric pressure and a temperature less than reflux temperature to produce the ester.
2. A method according to claim 1 comprising preparing the ester at ambient temperature.
3. A method according to claim 1 wherein the β -hydroxycarboxylic acid is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.
4. A method according to claim 1 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.
5. A method according to claim 1 wherein the alcohol contains between 1 and 7 carbon atoms, inclusive.
6. A method according to claim 1 wherein the esterification catalyst comprises an acid catalyst.
7. A method according to claim 6 wherein the acid catalyst comprises an acid resin catalyst.
8. A process for preparing a β -hydroxycarboxylic acid ester comprising: (a) providing a fermentation broth comprising a β -hydroxycarboxylic acid, or salt thereof; (b) forming a solution comprising the β -hydroxycarboxylic acid, or salt thereof, from the fermentation broth; and (c) reacting the β -hydroxycarboxylic acid, or salt thereof, with an alcohol in the presence of an esterification catalyst and the absence of solvent other than the alcohol under substantially anhydrous conditions at atmospheric pressure and a temperature less than reflux temperature to produce the ester.
9. A method for preparing a β -hydroxycarboxylic acid ester comprising reacting a β -hydroxycarboxylic acid with an alcohol containing between 1 and 7 carbon atoms,

inclusive, in the presence of an esterification catalyst in a water-immiscible extractant to produce a reaction mixture comprising the ester and the extractant.

10. A method according to claim 9 wherein the β -hydroxycarboxylic acid is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid,
5 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.
11. A method according to claim 9 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.
- 10 12. A method according to claim 9 wherein the water-immiscible extractant is selected from the group consisting of amides, ethers, ketones, phosphorus esters, phosphine oxides, phosphine sulfides, alkyl sulfides, and combinations thereof.
13. A method for preparing a β -hydroxycarboxylic acid ester comprising: (a) providing a fermentation broth comprising a β -hydroxycarboxylic acid, or salt thereof; (b) treating
15 the broth with a water-immiscible extractant to form an extract comprising the β -hydroxycarboxylic acid and the extractant; (c) combining the extract with an alcohol containing between 1 and 7 carbon atoms, inclusive, and an esterification catalyst; and (d) reacting the β -hydroxycarboxylic acid with the alcohol in the presence of the extractant and the catalyst to produce the ester.
- 20 14. A method for preparing an α,β -unsaturated carboxylic acid, or salt thereof, comprising: (a) providing an aqueous solution comprising a β -hydroxycarboxylic acid salt; and (b) heating the solution to dehydrate the salt and form an α,β -unsaturated carboxylic acid, or salt thereof.
15. A method according to claim 14 wherein the salt is selected from the group consisting
25 of alkali metal salts, alkaline earth metal salts, ammonium salts, and combinations thereof.
16. A method according to claim 14 wherein the salt comprises a sodium salt.
17. A method according to claim 14 wherein the salt comprises a calcium salt.
18. A method according to claim 14 wherein the β -hydroxycarboxylic acid is selected
30 from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-

methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.

19. A method according to claim 14 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.

5 20. A method according to claim 14 wherein the aqueous solution is derived from a fermentation broth.

21. A method according to claim 14 comprising heating the aqueous solution in the presence of a dehydration catalyst to dehydrate the salt and form an α,β -unsaturated carboxylic acid, or salt thereof.

10 22. A method according to claim 14 further comprising reacting the α,β -unsaturated carboxylic acid, or salt thereof, with an alcohol to form an α,β -unsaturated carboxylic acid ester.

23. A method for preparing an α,β -unsaturated carboxylic acid, or salt thereof, comprising: (a) providing a fermentation broth comprising a β -hydroxycarboxylic acid or salt thereof; (b) forming an aqueous solution comprising the β -hydroxycarboxylic acid, or salt thereof, from the fermentation broth; and (c) heating the aqueous solution to dehydrate the β -hydroxycarboxylic acid, or salt thereof, and form an α,β -unsaturated carboxylic acid, or salt thereof.

15 24. A method according to claim 23 wherein the β -hydroxycarboxylic acid is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.

20 25. A method according to claim 23 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.

26. A method according to claim 23 comprising heating the aqueous solution in the presence of a dehydration catalyst to dehydrate the β -hydroxycarboxylic acid, or salt thereof, and form an α,β -unsaturated carboxylic acid, or salt thereof.

27. A method according to claim 23 further comprising reacting the α,β -unsaturated carboxylic acid, or salt thereof, with an alcohol to form an α,β -unsaturated carboxylic acid ester.

28. A method for preparing an α,β -unsaturated carboxylic acid, comprising: (a) providing a fermentation broth comprising a β -hydroxycarboxylic acid; (b) forming a solution comprising the β -hydroxycarboxylic acid from the fermentation broth; and (c) vaporizing the solution in the presence of a dehydration catalyst to convert the β -hydroxycarboxylic acid to an α,β -unsaturated carboxylic acid.
29. A method according to claim 28 comprising adding the dehydration catalyst to the solution comprising the β -hydroxycarboxylic acid.
30. A method according to claim 28 comprising exposing the solution to a heated surface to vaporize the solution.
31. A method according to claim 30 wherein the heated surface comprises the dehydration catalyst.
32. A method according to claim 28 wherein the β -hydroxycarboxylic acid is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.
33. A method according to claim 28 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.
34. A method according to claim 28 wherein the β -hydroxycarboxylic acid is 3-hydroxy-2-methylpropionic acid.
35. A method according to claim 28 wherein the dehydration catalyst comprises an acid catalyst.
36. A method according to claim 28 further comprising converting the β -hydroxycarboxylic acid to an ester, and vaporizing a solution comprising the ester in the presence of the dehydration catalyst to convert the β -hydroxycarboxylic acid ester to an α,β -unsaturated carboxylic acid ester.
37. A method for preparing an α,β -unsaturated carboxylic acid ester comprising: (a) providing an aqueous solution comprising a β -hydroxycarboxylic acid or ester thereof, an alcohol, and a dehydration catalyst; and (b) heating the solution to form the α,β -unsaturated carboxylic acid ester.

38. A method according to claim 37 wherein the aqueous solution is derived from a fermentation broth.
39. A method according to claim 37 wherein the alcohol contains between 1 and 7 carbon atoms, inclusive.
- 5 40. A method according to claim 37 wherein the dehydration catalyst comprises an acid catalyst.
41. A method according to claim 37 wherein the β -hydroxycarboxylic acid is selected from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-
- 10 methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.
42. A method according to claim 37 wherein the β -hydroxycarboxylic acid is 3-hydroxypropionic acid.
43. A method of preparing an alkoxy derivative of a β -hydroxycarboxylic acid
- 15 comprising: (a) providing an aqueous solution comprising a β -hydroxycarboxylic acid, or salt thereof, an alcohol, and a basic catalyst in a closed reactor; and (b) heating the reactor to react the alcohol and the hydroxyl group of the β -hydroxycarboxylic acid to form an alkoxy derivative of the β -hydroxycarboxylic acid.
44. A method according to claim 43 wherein the catalyst is selected from the group
- 20 consisting of alkali metal hydroxides, alkali metal oxides, alkaline earth hydroxides, alkaline earth oxides, and combinations thereof.
45. A method according to claim 44 wherein the catalyst is selected from the group consisting of $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, NaOH , and combinations thereof.
46. A method according to claim 43 wherein the β -hydroxycarboxylic acid is selected
- 25 from the group consisting of 3-hydroxypropionic acid, 3-hydroxy-2-methylpropionic acid, 3-hydroxybutanoic acid, 3-hydroxy-2-methylbutanoic acid, 3-hydroxy-2-methylpentanoic acid, 3-hydroxy-3-methylbutanoic acid, 2,3-dimethyl-3-hydroxybutanoic acid, 3-hydroxy-3-phenylpropionic acid, and combinations thereof.
47. A method according to claim 43 wherein the β -hydroxycarboxylic acid is 3-
- 30 hydroxypropionic acid.

48. A method according to claim 43 wherein the aqueous solution is derived from a fermentation broth.

49. A method for preparing an α,β -unsaturated carboxylic acid ester comprising heating a solution comprising a β -hydroxycarboxylic acid, an alcohol containing between 1 and 7 carbon atoms, inclusive, and a water-immiscible solvent to form the α,β -unsaturated carboxylic acid ester.

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